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(54) Title: POLYMERIZATION PROCESS FOR PRODUCING COPOLYMERS

(57) Abstract: The invention provides a process for the preparation of a propylene polymer in which propylene and a comonomer copolymerizable therewith and of greater molecular weight than propylene are polymerized in a single site catalyst catalyzed polymerization reaction,, characterised in that said polymerization reaction is effected at least in part at a temperature of at least 70° C.

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Chem. Phys. 201: 401-408 (2000)).

Moreover polypropylenes produced using single site, eg metallocene, catalysts tend to have a narrower molecular weight distribution than those produced using  
5 Ziegler-Natta catalysts resulting in corresponding poor melt strengths. As melt strength is important for applications involving extrusion, blow molding, pipe, film or sheet formation, etc., this is a further disadvantage for single site catalyst based  
10 polypropylenes.

We have now surprisingly found that by carrying out the polymerization reaction at unusually high temperatures the comonomer incorporation rate can be increased to become comparable to or even greater than  
15 that of propylene, and that long chain branching (which increases melt strength) occurs, thus addressing the disadvantages discussed above.

Thus according to one aspect the invention provides a process for the preparation of a propylene polymer in  
20 which propylene and a comonomer copolymerizable therewith and of greater molecular weight than propylene are polymerized in a single site catalyst (typically an organotransition metal catalyst (eg a metallocene catalyst)) catalysed polymerization reaction,  
25 characterised in that said polymerization reaction is effected at least in part (e.g. for at least 5%, for example 10 to 100% of the polymerization time or of the average residence time in a continuous reactor) at a temperature of at least 70°C.

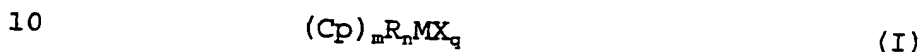
30 In the process of the invention, the polymerization reaction is preferably effected at from 75 to 200°C, more preferably 80 to 125°C, still more preferably 85 to 120°C.

The higher molecular weight comonomer used in the  
35 process of the present invention is preferably an alkene or diene, in particular a C<sub>4-30</sub> alkene or diene (e.g. a C<sub>4-20</sub> α-olefin or diene, such as 7-methyl-1,6-octadiene or

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particularly preferably is a titanocene, zirconocene or hafnocene, and contains at least one  $\eta^5$ -ligand, which is for example an optionally substituted cyclopentadienyl, an optionally substituted indenyl, an optionally substituted benzoindenyl, an optionally substituted azulenyl or an optionally substituted fluorenyl.

The metallocene compound may thus for example be of formula I:



wherein each Cp independently is an unsubstituted or substituted and/or fused homo- or heterocyclopentadienyl ligand (e.g. substituted or unsubstituted cyclopentadienyl, substituted or unsubstituted indenyl, substituted or unsubstituted benzoindenyl, substituted or unsubstituted azulenyl, substituted or unsubstituted fluorenyl ligand, substituted or unsubstituted indolyl, or substituted or unsubstituted 4-azaindenyl, the optional one or more substituent(s) being selected preferably from halogen, hydrocarbyl (e.g.  $C_{1-20}$ -alkyl,  $C_{2-20}$ -alkenyl,  $C_{2-20}$ -alkynyl,  $C_{3-12}$ -cycloalkyl,  $C_{6-20}$ -aryl or  $C_{7-20}$ -arylalkyl),  $C_{3-12}$ -cycloalkyl which contains 1, 2, 3 or 4 heteroatom(s) in the ring moiety,  $C_{6-20}$ -heteroaryl,  $C_{1-20}$ -haloalkyl,  $-SiR''_3$ ,  $-OSiR''_3$ ,  $-SR''$ ,  $-PR''_2$  or  $-NR''_2$  (where each  $R''$  is independently hydrogen or a hydrocarbyl group (e.g.  $C_{1-20}$ -alkyl,  $C_{2-20}$ -alkenyl,  $C_{2-20}$ -alkynyl,  $C_{3-12}$ -cycloalkyl,  $C_{6-20}$ -aryl or  $C_{7-10}$  arylalkyl), or, for example in the case of  $-NR''_2$ , two substituents  $R''$  can form a ring, e.g. a five- or six-membered ring, together with the nitrogen atom they are attached to);

R is a bridge of 1-7 atoms, e.g. a bridge of 1-4 C-atoms and 0-4 heteroatoms, wherein the heteroatom(s) can be e.g. Si, Ge, O, S, N, P and/or B atom(s), whereby each of the bridge atoms may independently bear substituents, such as  $C_{1-20}$ -alkyl, tri( $C_{1-20}$ -alkyl)silyl, tri( $C_{1-20}$ -alkyl)siloxy or  $C_{6-20}$ -aryl substituents), or a

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- rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_2\text{CH}_3\text{-4-(4-tertbutyl-phenyl)-indenyl})_2\text{ZrCl}_2$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}(\text{CH}_3)_2\text{-4-phenyl-indenyl})_2\text{ZrCl}_2$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}(\text{CH}_3)_2\text{-4-(1-naphthyl)-indenyl})_2\text{ZrCl}_2$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}(\text{CH}_3)_2\text{-4-(4-tertbutyl-phenyl)-indenyl})_2\text{ZrCl}_2$   
 5 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}(\text{CH}_3)_2\text{-4-(2-CH}_3\text{-phenyl)-indenyl})_2\text{ZrCl}_2$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}(\text{CH}_3)_2\text{-4-(3,5-(CH}_3)_2\text{-phenyl)-indenyl})_2\text{ZrCl}_2$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{ZrCl}(\text{CH}_3)$   
 10 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{ZrCl}(\text{NMe}_2)$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{ZrCl}(\text{O-phenyl})$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{ZrCl}(\text{NEt}_2)$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{ZrCl}(\text{NPr}_2)$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{Zr}(\text{NMe}_2)_2$   
 15 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{Zr}(\text{NEt}_2)_2$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{Zr}(\text{NPr}_2)_2$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{Zr}(\text{CH}_3)_2$   
 rac- $(\text{CH}_3)_2\text{Si}(2\text{-CH}_3\text{-4-phenyl-indenyl})_2\text{Zr}(\text{O-phenyl})_2$   
 rac- $(\text{CH}_3)_2\text{C}(3\text{-tertbutyl-indenyl})_2\text{ZrCl}_2$  and  
 20 rac- $\text{CH}_2(3\text{-tertbutyl-indenyl})_2\text{ZrCl}_2$

Alternatively, in a further subgroup of the metallocene compounds, the metal bears a Cp group as defined above and additionally a  $\eta^1$  or  $\eta^2$  ligand, wherein said ligands may or may not be bridged to each other.  
 25 This subgroup includes so called "scorpionate compounds" (with constrained geometry) in which the metal is complexed by a  $\eta^5$  ligand bridged to a  $\eta^1$  or  $\eta^2$  ligand, preferably  $\eta^1$  (for example a  $\sigma$ -bonded) ligand, e.g. a metal complex of a Cp group as defined above, e.g. a  
 30 cyclopentadienyl group which bears, via a bridge member, an acyclic or cyclic group containing at least one heteroatom, e.g.  $\text{-NR}_2$ , as defined above. Such compounds are described e.g. in WO-A-96/13529, the contents of which are incorporated herein by reference.

35 Any alkyl, alkenyl or alkynyl residue referred to above alone or as a part of a larger moiety may be linear or branched, and preferably contains up to 9,

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then metalling said organic ligand ( $\eta$  ligand) with a transition metal. Alternatively, a metal ion of an existing metallocene can be exchanged for another metal ion through transmetallation.

5       As is conventional the metallocene may be used together with a cocatalyst or catalyst activator. Preferred as cocatalysts for metallocenes are the alumoxanes, in particular the  $C_{1-10}$  alkylalumoxanes, most particularly methylalumoxane (MAO). Such alumoxanes can  
10       be used as the sole cocatalyst or together with other cocatalyst(s). Thus besides or in addition to alumoxanes, other cation complex forming activators can be used. In this regard mention may be made particularly to boron compounds known in the art. Said  
15       activators are commercially available or can be prepared according to the prior art literature.

      Further alumoxane cocatalysts are described i.a. in WO-A-94/28034 which is incorporated herein by reference. These are linear or cyclic oligomers having up to 40,  
20       preferably 3 to 20,  $-(Al(R''')O)-$  repeat units (wherein  $R'''$  is hydrogen,  $C_{1-10}$  alkyl (preferably methyl) or  $C_{6-18}$  aryl or mixtures thereof).

      The quantity of cocatalyst to be employed in the catalyst of the invention is thus variable, and depends  
25       on the conditions and the particular transition metal compounds chosen in a manner well known to a person skilled in the art.

      The metallocene used in the process of the invention may be used as a homogeneous or, more preferably a heterogeneous catalyst. Thus it is.  
30       preferably impregnated into a porous particulate catalyst support which may be organic or more preferably inorganic, e.g. silica, silica-alumina, etc. Where the catalyst is used with a cocatalyst or catalyst activator  
35       (generally an aluminium or boron containing compound, e.g. an organoaluminium compound (such as an alumoxane) or a non-coordinating ionic cocatalyst such as a boron

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continuous or batch mode. Conventional polymerisation reactors, e.g. loop or stirred tank or gas phase reactors, may be used and if desired polymerisation may be effected in more than one stage and/or in more than one reactor.

If desired, hydrogen may be used as a chain transfer agent in the polymerization reaction.

Moreover, a scavenger may be included in the reaction mixture, for example an organoaluminium compound, eg a trialkylaluminium such as triethylaluminium (TEAL) or triisobutylaluminium (TIBAL) or an alumoxane (such as MAO, TIBAO, HIBAO, etc).

Long chain branching of propylene polymers results in improved melt strength. Generally this has only been achievable for propylene polymers by post-reactor modification, e.g. peroxide or silane treatment or irradiation with ionizing radiation such as electron beams (see for example WO00/63287). We have now found that by performing metallocene catalysed propylene polymerisation at temperatures above 70°C, especially above 75°C, more particularly above 80°C (i.e. according to the invention), significant long chain branching occurs. This is evidenced by the flow activation energies of the polymer product.

The flow activation energy ( $E_a$ ), which represents the temperature dependence of the viscosity of the polymer melt, is sensitive to the presence of long chain branches in the polymer backbone. A higher flow activation energy can be related to the growing number of long branches. Flow activation energy values of up to about 40 kJ/mol have been reported in the literature for linear polypropylene homopolymers or random copolymers (see Mavridis et al. in Polym. Eng. Sci. 32:1778-1791 (1992)). Descriptions of flow activation energies and their determination may also be found for example in Mavridis et al. (supra), Eckstein et al. Macromolecules 31:1335-1340 (1998), and Saini et al. J.

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The invention will now be illustrated further with reference to the following non-limiting Examples.

The silica-supported catalysts used in the Examples were prepared as described in WO 95/12622.

5 In the Examples, the following measurement techniques were used.

#### NMR

10 Incorporated comonomer contents were determined by nuclear magnetic resonance spectroscopy (NMR) from a quantitative proton-decoupled (NOE)  $^{13}\text{C}$  spectra obtained at 120-130°C on a CMX 400 Infinity (400 MHz) or a Varian Gemini 2000 (300 MHz) spectrometer from samples dissolved in 1,2,4-trichlorobenzene/benzene- $\text{d}_6$ . The  
15 interpretation of spectra was made on the basis of the spectral assignments found in the literature of copolymers of higher olefins with propylene (see Cheng in Polym. Commun. 25:99-105 (1984)).

#### 20 GPC

Weight average ( $M_w$ ) and number average ( $M_n$ ) molecular weights were measured with a Waters Alliance GPCV 2000 high temperature gel permeation chromatograph (GPC) operating at 140°C using 1,2,4-trichlorobenzene as an  
25 eluant. The calibration of columns was done with polystyrene standards and polypropylene equivalent molecular weights were calculated using a universal calibration method.

#### 30 DSC

The thermal behaviour of copolymers, melting temperatures ( $T_m$ ) and glass transition temperatures ( $T_g$ ), were determined by differential scanning calorimetry (DSC) according to ISO 11357.  $T_m$  was measured as peak  
35 temperature from second melting endotherm at a heating rate of 10°C/min. Indium was used for the calibration of the temperature scale.

Table 1

Example	Comonomer	Comonomer (g)	Propene (g)	Run Temperature (°C)	Comonomer Content mol %		M <sub>w</sub> <sup>c</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>c</sup>	T <sub>m</sub> <sup>f</sup> (°C)	E <sub>a</sub> (kJ/mol)
					Feed <sup>a</sup>	Polymer <sup>b</sup>				
1 <sup>e</sup>	1-hexene	29.9	1500	60	1.0	0.8	697	2.4	138.5	40.3
2	1-hexene	28.1	1400	70	1.0	1.0	667	2.4	136.0	38.6
3	1-hexene	19.3	1300	80	0.7	1.0	562	2.1	135.2	51.8
4	1-hexene	24.2	1200	90	1.0	1.3	418	2.5	134.9	58.6
5	1-hexene	20.2	1000	100	1.0	1.6	374	3.4	130.2	80.8
6	1-hexene	62.0	1200	90	2.5	3.1	300	3.3	117.3	
7	1-hexene	50.0	1000	100	2.4	3.8	238	3.1	113.3	43.9
8	4-Me-1-pentene	24.0	1200	90	1.0	1.0	308	2.5	137.5	
9	4-Me-1-pentene	24.0	1000	100	1.2	1.2	192	3.2	134.1	
10	1-octene	32.5	1200	90	1.0	1.5	362	2.7	132.7	
11	1-octene	26.5	1000	100	1.0	2.2	200	3.1	126.2	47.3
12 <sup>d</sup>	1-hexene	23.9	1200	90	1.0	1.3	697	2.9	133.2	

a) initial comonomer content in polymerization medium

b) calculated by <sup>13</sup>C NMR

c) comparative example

d) Examples 1 to 11 used catalyst A, Example 12 catalyst B

+ ) calculated by GPC

\* ) calculated by GPC

# ) calculated by DSC



Table 2

Examples	Comonomer	Feed (mol-%)	Polymer <sup>a</sup> (mol-%)	M <sub>w</sub> <sup>b</sup> (kg/mol)	M <sub>w</sub> /M <sub>n</sub> <sup>b</sup>	T <sub>m</sub> <sup>c</sup> (°C)	T <sub>g</sub> <sup>c</sup> (°C)
5	1-butene	5	4.3	460	2.1	140	-8
		8	7.6			135	-9
		12	11.2	258	2.1	119	-12
		15	12.8	239	2.1	110	-14
10	1-hexene	2	3.1			126	-7
		4	4.0	336	2.1	110	-10.5
		8	8.9	183	2.5	73	-15
		15	14.7	169	2.0	47	-18
		20	20.5			40	-19
15	1-octene	2	2.6	257	2.3	120	-9
		8	7.7	196	2.1	81	-19
		10	10.2	165	1.9	66	-22
		20	20.2				-27
	1-dodecene	8	9.1	192	2.0		-35
		15	17.0				-39
20	1-hexadecene	8	7.5	169	2.0		
		15	14.0				-45

<sup>a</sup>) <sup>13</sup>C NMR, <sup>b</sup>) GPC, <sup>c</sup>) DSC

In the copolymerizations conducted at 70°C in the liquid monomer mixture the compositions of the produced copolymers are near to identical to the corresponding monomer compositions in the polymerization medium, even in the case of the higher molecular weight comonomers like 1-dodecene and 1-hexadecene.

#### EXAMPLES 30-37

Polymerization experiments were carried out in a PARR 600-ml steel autoclave. The polymerization medium (250

Claims:

1. A process for the preparation of a propylene polymer in which propylene and a comonomer  
 5 copolymerizable therewith and of greater molecular weight than propylene are polymerized in a single site catalyst catalysed polymerization reaction, characterised in that said polymerization reaction is effected at least in part at a temperature of at least  
 10 70°C.

2. A process as claimed in claim 1 wherein said single site catalyst is a metallocene.

15 3. A process as claimed in claim 2 wherein said metallocene is of formula I



20 wherein each Cp independently is an unsubstituted or substituted and/or fused homo- or heterocyclopentadienyl ligand

R is a bridge of 1-7 atoms;

M is a transition metal of group 3 to 6, a  
 25 lanthanide or an actinide;

each X is independently a sigma-ligand;

n is 0, 1 or 2;

m is 1, 2 or 3;

q is 1, 2 or 3; and

30 the sum of m and q is equal to the valency of M.

4. A process as claimed in claim 3 wherein said metallocene is selected from  
 rac-(CH<sub>3</sub>)<sub>2</sub>Si(2-CH<sub>3</sub>-4-phenyl-indenyl)<sub>2</sub>ZrCl<sub>2</sub>  
 35 rac-(CH<sub>3</sub>)<sub>2</sub>Si(2-CH<sub>3</sub>-4-phenyl-indenyl)<sub>2</sub>TiCl<sub>2</sub>  
 rac-(CH<sub>3</sub>)<sub>2</sub>Si(2-CH<sub>3</sub>-4-phenyl-indenyl)<sub>2</sub>HfCl<sub>2</sub>  
 rac-(CH<sub>3</sub>)<sub>3</sub>Si(CH<sub>3</sub>)Si(2-CH<sub>3</sub>-4-phenyl-indenyl)<sub>2</sub>ZrCl<sub>2</sub>

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8. A process as claimed in any one of claims 1 to 7 wherein said polymerization reaction is effected at least in part under supercritical conditions.
- 5 9. A process as claimed in any one of claims 1 to 8 wherein said comonomer is selected from C<sub>4-30</sub> alkenes and dienes.
- 10 10. A process as claimed in claim 9 wherein said comonomer is a C<sub>4-16</sub> alkene.
- 15 11. A process as claimed in any one of claims 1 to 10 wherein said polymerisation reaction is effected in at least two stages.
12. A propylene polymer produced or producible by a process according to any one of claims 1 to 11.
- 20 13. A propylene copolymer having on polymerization a flow activation energy of at least 43 kJ/mol.
- 25 14. A copolymer as claimed in claim 13 having on polymerization a flow activation energy of 45 to 90 kJ/mol.
15. A propylene polymer article formed from a polymer according to any one of claims 12 to 14 optionally after formulation thereof.
- 30 16. The use of a copolymer as claimed in any one of claims 12 to 14 for the manufacture of pipe, film, sheet, fibre, molded articles and foamed articles.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 02/02057

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08F210/06 C08F2/14

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 29742 A (EXXON CHEMICAL PATENTS INC) 17 June 1999 (1999-06-17) abstract page 3, line 15 -page 5, line 7 page 6, line 19 -page 7, line 6 page 8, line 17 - line 30 page 15, line 19 - line 23 page 19, line 18 -page 21, line 17 page 22, line 18 - line 28; claims 18-22; examples	1-16
X	US 6 084 041 A (PENTTI ISMO ET AL) 4 July 2000 (2000-07-04) abstract column 2, line 30 -column 3, line 37 column 3, line 40 -column 4, line 61 column 5, line 35 -column 6, line 21 claims; examples	1-16

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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